

Fine chemicals from larch wood biomass

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Introduction

Such features of larch wood, as an increased content of extractive compounds and its high density create some technological problems for pulping process. It seems that a production of high-value added chemicals is a most profitable from economical point of view way of larch wood valorization. Up to present mainly the production of arabinogalactan and quercetin dihydrate from larch wood was suggested [1].

The goal of this work is to study new ways of wasteless processing of larch wood into a number of high value organic compounds: arabinogalactan (AG), quercetin dihydrate (QDH), vanillin (V), microcrystalline cellulose (MCC) and levulinic acid (LA).

Experimental

The size of wood particles was varied in the following range: shaving 30?10?1 min, sawdust: 2-5 mm and 2-0,5 mm. The chemical composition of used larch wood(% wt. on a.d.w.): cellulose 34.5, lignin 26.1, hemicellulose 27.2 extractive substances 13.

Arabinogalactan and quercetin dihydrate were isolated by extraction of wood fraction with hot water according to procedure described in [2]. Microcrystalline cellulose was obtained by organosolvent pulping of extracted wood in a static reactor by pulping liquor: 30% CH₃COOH + 35% H₂O₂ (H₂O₂/CH₃COOH=0.5) + 2% H₂SO₄ at 130°C and liquor/wood ratio 15:1 during 3 h. Wood oxidation to vanillin and cellulose was carried out in flow reactor at 170 °C, working pressure 0.5 MPa in an alkaline medium in the presence of copper catalyst (CuSO₄). The used procedure was described in [3]. The oxidation step gives two main products: cellulose and water solution of vanillin. Levulinic acid was produced at the second step of the process by acid-catalysed conversion of cellulose at 200°C in the presence of H₂SO₄ (5% wt.).

Results and discussion

Isolation of AG and QDH

Both AG and QDH were extracted from larch wood with boiling water. The variation of extraction process operating parameters (time, water/wood ratio, temperature and wood particle sizes) on the yield of AG and QDH was investigated in order to reach the optimum yield of these products. Obtained data show that the maximum yields of both AG and QDH correspond to the time extraction 60 min. The amounts of AG and QDH extracted by water were also depended on the water/wood ratio. The maximum yields of AG (18.50 % wt.) and QDH (0.59% wt.) for fraction of wood 0.5-2.0 mm was observed at water/wood ratio 8:1. The lower yield of QDH at water/wood ratio 10:1 (0.28% wt.) can be explained by its significant loss during desorption from polyamide sorbent with high amount of water. For the fraction of wood with larger size of particles (2-5 mm) the maximum yield of AG (17.11% wt.) was also observed at water/wood ratio 8:1 and time 60 min. Higher water/wood ratios and higher times of extraction increase the total amount of extracted substances but probably promote the hydrolysis of AG in water solution decreasing its yield.

According to obtained data the yields of water-soluble substances and AG were increased with temperature rising from 20°C to 100°C. The optimum parameters of AG isolation corresponding to its highest yield (18.5% wt.) are temperature 100°C and time 60 min. For wood fraction 2-5 mm the yield of AG was increased from 9.72% wt. to 13.39% wt. with extraction temperature growth in interval 20-100°C. Suggested in [1] procedure of AG isolation includes the larch wood pre-treatment with organic

solvent (ethylacetate, hexane, benzol) and following extraction by boiling water AG with yield about 10% wt. and QDH with yield around 0.6% wt.

The another known way of wood activation is a short-time treatment by steam with the following fast drop of a pressure [4]. This treatment produces a friable material which is more accessible for extractants then non-treated wood. It was shown that the treatment of larch-wood chips by steam at 200 and 220°C during 3 min results in the formation of high amount of water-soluble substances (43.19 and 35.28% wt. respectively). But this activation treatment decreases the yield of AG obviously as a result of its hydrolytic degradation under the action of organic acids formed from carbohydrates under the process conditions.

Integrated process of larch wood

Two integrated processes of larch wood valorization into fine chemicals have been investigated. One of them is based on the combination of following steps: extractive isolation of AG and QDH from wood, organosolvent pulping of extracted wood with producing microcrystalline cellulose and low-molecular-mass lignin. The yield of products (% wt. on a.d.w.): arabinogalactan 18.1, quercetin dehydrate 0.6, microcrystalline cellulose 20.9, soluble lignin 11.9.

AG is used for sizing and forming of paper, cardboard and for improvement of their quality, as filler in pills and tablets production, etc. QDH has antioxidant, antiphlogistic and antihistamine properties. Therefore it has found an application in medicine. MCC is widely used as filtering, auxiliary and filling material in metallurgy, plastics, food industries, in medicine and pharmaceuticals and other fields. Soluble lignin can be used as a partial substitute of phenols in phenolic resins and plastic industry. The another studied way of larch wood conversion into fine chemical is based on the steps of AG and QDH extraction by water with following oxidation of extracted wood by molecular oxygen in alkaline medium with formation of vanillin and cellulose, and cellulose conversion to levulinic acid. The yield of products (% wt. on a.d.w.): AG 18.1, QDH 0.6, vanillin 5.4, levulinic acid 8.6.

LA is used in medicine (Ca levulinate), for plastics and fine chemicals production and in other fields.

Acknowledgement

The research was funded in part by European Commission in the framework of INCO-COPERNICUS program, Contract No ERBIC 15 CT98 0804.

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